

Terpene and Steroid Alkynyl Peroxides

E. A. Dikusar¹, N. G. Kozlov¹, K. L. Moiseichuk¹,
and A. P. Yuvchenko²

¹Institute of Physical Organic Chemistry, Belorussian National Academy of Sciences, Minsk, 220072 Belarus

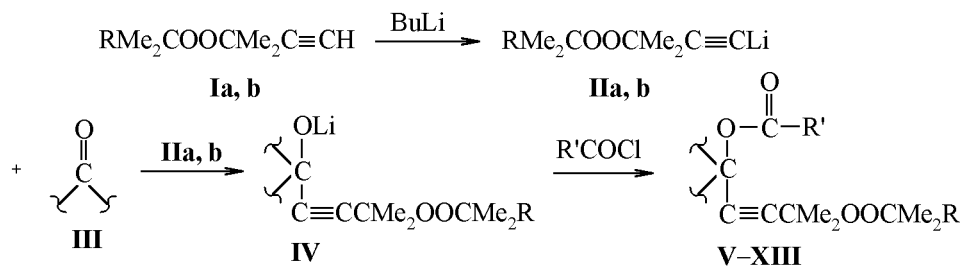
²Institute of New Material Chemistry, Belorussian National Academy of Sciences, Minsk, 220141 Belarus

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Abstract—A method was developed for preparation of alkynyl peroxides from terpene and steroid aldehydes and ketones by reaction of lithium peroxyacetylides with the corresponding aldehydes and ketones followed by treating the intermediate lithium alcoholates with acyl chlorides.

In [1-3] we reported on the synthesis of alkynyl peroxides of camphor, isocamphanone, 1-menthone, and esters based thereon. In the present paper we describe the syntheses of alkynyl peroxides proceeding from terpene and steroid aldehydes and ketones

III: 6-methyl-4-(4-methylpent-3-enyl)cyclohex-3-enecarbaldehyde (**IIIa**), 2-acetyl-2,3,5,8-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalene (**IIIb**), ethyl 3,4-dimethoxyphenyl ketone (**IIIc**), 2,2-dimethyltetrahydro-4H-pyran-4-one (**IIId**), cholest-4-en-3-one



R = Et (**a**), Pr (**b**); R' = Me, (CH₂)₆Me, C(Me)=CH₂, Ph.

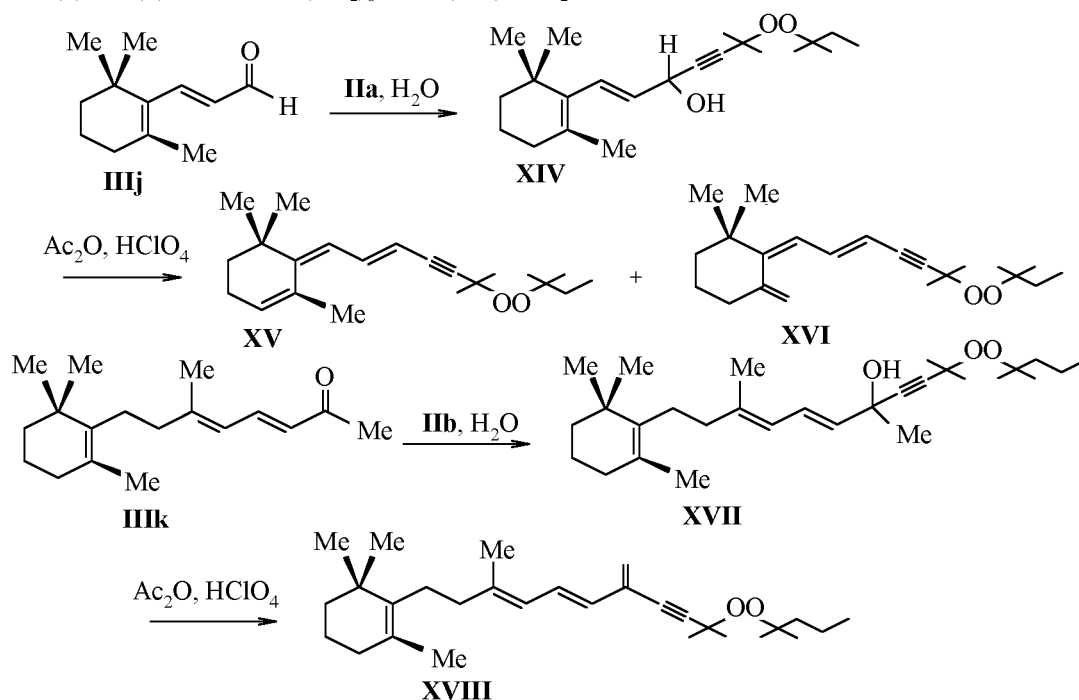


Table 1. Characteristics of peroxy-containing esters **V**, **b**, **VIa, b**, **VII–IXa–c**, **X–XII**, **XIII** **–e**, alcohols **XIV**, **XVII**, and tetraenyne **XVIII**

Compd. no.	Yield, %	d_{20}^{20}	n_D^{20}	Found, %		Formula	Calculated, %		<i>M</i>	
				C	H		C	H	found	calcd.
Va	67	1.1079	1.4785	76.36	10.25	C ₂₉ H ₄₆ O ₄	75.94	10.11	450.0	458.7
Vb	78	1.1629	1.5045	78.03	9.58	C ₃₂ H ₄₆ O ₄	77.69	9.37	480.3	494.7
VIa	75	1.1038	1.4860	76.94	10.41	C ₃₁ H ₅₀ O ₄	76.50	10.35	477.1	486.7
VIb	70	1.1321	1.5125	78.25	9.68	C ₃₃ H ₄₈ O ₄	77.91	9.51	499.4	508.7
VIIa	66	1.1392	1.5040	70.41	8.66	C ₂₆ H ₃₈ O ₆	69.93	8.58	441.0	446.6
VIIb	71	1.0416	1.4800	71.84	9.73	C ₃₀ H ₃₈ O ₆	71.39	9.59	494.7	504.7
VIIc	69	1.1701	1.5250	72.84	8.20	C ₂₉ H ₃₈ O ₆	72.17	7.94	470.6	482.6
VIIIa	70	1.1567	1.4655	69.15	9.70	C ₂₁ H ₃₄ O ₅	68.82	9.35	356.5	366.5
VIIIb	75	1.0524	1.4545	70.95	10.60	C ₂₅ H ₄₄ O ₅	70.72	10.44	417.0	424.6
VIIIc	84	1.1388	1.4985	72.63	8.88	C ₂₅ H ₃₆ O ₅	72.09	8.71	403.8	416.6
IX	63	1.0868	1.5045	78.81	10.94	C ₃₉ H ₆₄ O ₄	78.47	10.81	584.1	596.3
IXb	62	1.0389	1.5040	79.51	10.83	C ₄₁ H ₆₆ O ₄	79.05	10.68	606.3	623.0
IXc	70	1.1791	1.5200	80.77	10.33	C ₄₄ H ₆₆ O ₄	80.19	10.09	649.3	659.0
X	69	1.1477	1.4935	74.80	9.71	C ₃₇ H ₅₆ O ₆	74.46	9.46	588.4	596.8
XI	63	1.2341	1.4840	73.41	10.03	C ₃₄ H ₅₄ O ₆	73.08	9.74	544.3	558.8
XII	66	1.1786	1.5105	75.60	9.14	C ₃₈ H ₅₄ O ₆	75.21	8.97	600.3	606.8
XIIIa	79	1.1849	1.5120	75.18	8.50	C ₃₆ H ₄₈ O ₆	74.97	8.39	560.3	576.8
XIIIb	81	1.1607	1.5100	75.24	8.57	C ₃₇ H ₅₀ O ₆	75.22	8.53	581.0	590.8
XIIIc	71	1.2489	1.4795	76.84	10.13	C ₄₄ H ₆₈ O ₆	76.26	9.89	677.2	693.0
XIII d	68	1.1298	1.4820	76.90	10.11	C ₄₅ H ₇₀ O ₆	76.44	9.98	688.4	707.0
XIII e	69	mp 150–151		77.91	7.55	C ₄₂ H ₄₈ O ₆	77.75	7.46	626.4	648.8
XIV	92	1.0895	1.4890	76.13	10.60	C ₂₂ H ₃₆ O ₃	75.82	10.41	338.0	348.5
XVII	82	1.0797	1.5095	78.41	10.93	C ₂₉ H ₄₈ O ₃	78.33	10.88	432.3	444.7
XVIII	53	1.0206	1.5285	82.16	10.99	C ₂₉ H ₄₆ O ₂	81.63	10.87	409.8	426.7

(**IIIe**), 17 β -hydroxyandrostane-3-one (**III f**), 3 β -hydroxy-5 α -androstane-17-one (**III g**), 17 β -hydroxyandrostane-1,4-diene-3-one (**III h**), and 3-hydroxyestra-1,3,5(10)-trien-17-one (**III i**). The synthesis procedure consists in reaction of lithium peroxyacetylides **IIa, b** with terpene and steroid aldehydes and ketones **III** followed by treatment of intermediately formed lithium alcoholates **IV** with acetyl, octanoyl, methacryloyl, and benzoyl chlorides. As a result were obtained peroxyalkynyl esters **V–XIII** in 62–84% yield. Esters **V–XIII** may be of interest as biologically active compounds [4–7].

Compounds **V–XIII** are easily prepared by two-stage synthesis without separation of intermediately arising lithium acetylides **II** and alcoholates **IV**. The target peroxides **V–XIII** were purified by column chromatography. Compounds **Va, b–VIIIa–c** prepared from terpene aldehydes and ketones were isolated in individual state. Peroxides **IXa–c–XIIIa–e** obtained from ketosteroids are mixtures of α - and β -isomers with respect to 3 position (**IXa–c, X, XII**)

and 17 position (**XI, XIIIa–e**) of steroid core in ~2:3 ratio according to ¹H and IR spectra. The prevailing isomer possesses α -located C \equiv CCMe₂OOCMe₂R group due to weak shielding effect of two β -Me groups in positions 10 and 13 [6]. The like behavior was observed at the synthesis of peroxy derivatives of 1-menthone [3].

At the use of 3-(2,6,6-trimethylcyclohex-1-enyl)-2-propenal (**III j**) and 6-methyl-8-(2,6,6-trimethylcyclohex-1-enyl)-octa-3,5-dien-2-one (**III k**) as the initial carbonyl compounds the stage of the process resulting in lithium peroxyalkynyl alcoholates (**IV**) proceeded cleanly. However the latter as the derivatives of 1-acetyladamantane [8] do not yield the target esters when treated with acyl chlorides. The hydrolysis of lithium alcoholates with water afforded alcohols **XIV** and **XVII** in 92 and 82% yield respectively. Yet the attempt to acylate alcohols **XIV** and **XVII** with acetic anhydride in the presence of catalytic amount of HClO₄ led to dehydration of the alcohols accompanied by isomerization. As a result from alcohol

XIV formed a mixture of trienynes **XV** and **XVI** in ~1:1 ratio in overall yield 59%. We failed to separate the components of the mixture since they are prone to polymerization. Peroxyalcohol **XVII** gave rise to tetraenyne **XVIII** in 53% yield.

Peroxyesters **Va, b-XIIIa-d**, alcohols **XIV, XVII**, and tetraenyne **XVIII** are colorless or lightly colored viscous fluids soluble in the common organic solvents and insoluble in water. Compound **XIIIe** is crystalline. The peroxides are stable at storage in the dark at -10...-15°C; at long storage they should be protected with hydroquinone. The peroxides were purified by column chromatography on Al₂O₃ (compounds **Va, b-XIIIa-e, XV, XVI, XVIII**) or on silica gel (compounds **XIV, XVII**) with subsequent keeping in vacuo. Compound **XIIIe** was recrystallized from hexane.

The composition and structure of compounds **Va, b-XIIIa-e, XIV, XVII, XVIII** synthesized were confirmed by elemental analysis, molecular weight measurement (Table 1), IR, ¹H NMR (Table 2), and UV (Table 3) spectra.

In the IR spectra of peroxides **Va, b-XIIIa-e, XIV, XVII, XVIII**, and those of the mixture of compounds **XV, XVI** are lacking the absorption bands $\nu(\equiv\text{CH})$ of the initial peroxyalkynes **Ia, b**, and $\nu(\text{C}=\text{O})$ of aldehydes and ketones **III** [9]. In the IR spectra of esters **V-XIII** are no bands of $\nu(\text{OH})$, but appear the absorption bands of stretching vibrations $\nu(\text{C}=\text{O})$ at $1740\pm 20\text{ cm}^{-1}$. In the IR spectra of methacrylates **Va, VIa, VIIa, VIIIa, X, XII, XIIIa, b** are present the bands of stretching vibrations of

$\text{C}=\text{C}$ and $=\text{C}-\text{H}$ bonds at 1640 ± 15 and $3105\pm 10\text{ cm}^{-1}$ respectively, and in the IR spectra of benzoates **Vb, VIb, VIIc, VIIIc, XIIIe** are observed absorption bands of $\text{C}-\text{H}$ arom at 3100 ± 5 , 3075 ± 5 , 3040 ± 5 , $705\pm 10\text{ cm}^{-1}$ and skeletal vibrations of the benzene ring at 1600 ± 5 and $1580\pm 5\text{ cm}^{-1}$. IR spectra of peroxides originating from unsaturated compounds **Va, b, VIa, b, IX, XII, XIV-XVIII** contain the absorption bands of $\text{C}=\text{C}$ bonds at $1630\pm 30\text{ cm}^{-1}$. In the IR spectra of aromatic compounds **VIIa-c** appear the absorption bands at 3075 ± 5 , 1605 ± 5 , 1595 ± 10 , 1525 ± 5 , 805 ± 5 , $770\pm 5\text{ cm}^{-1}$, of compounds **XVa-e** at 3050 ± 5 , 1620 ± 5 , 1580 ± 5 , 1505 ± 5 , 820 ± 5 , $790\pm 5\text{ cm}^{-1}$. In the IR spectra of peroxyalcohols **XIV, XVII** are present the absorption bands of stretching vibrations of associated hydroxy groups at $3425\pm 5\text{ cm}^{-1}$.

Initial compounds **III** were supplied by Prof. V. G. Kartsev (INTERBIOSCREEN Co, Moscow).

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from samples prepared as thin films or KBr pellets (**XVe**). ¹H NMR spectra were registered on spectrometer Tesla BS-567A in CDCl₃, internal reference TMS. UV spectra were measured on spectrophotometer Specord UV Vis from solutions of compounds in methanol at $1\times 10^{-4}\text{ M}$ concentration. The homogeneity of compounds was checked by TLC on Silufol plates 20 cm high, eluent hexane-ethyl ether (3:1), development with *N,N*-dimethyl-*p*-phenylenediamine hydrochloride. Compounds synthesized contained no less than 90-95% of the

Table 2. ¹H spectra of compounds **Va, b, VIa, b, VII-IXa-c, X-XII, XIIIa-e, XIV, XVII, XVIII**

Compd. no.	δ , ppm
Va	0.80-1.10 m (3H, Me), 1.18 s (6H, Me ₂ COO), 1.25-2.25 m [15H, 3CH, 2CH ₂ and 2(CH ₂) ₂], 1.42 s (6H, Me ₂ CC≡C), 1.52 s (3H, CHMe), 1.60 s and 1.67 s (6H, Me ₂ C=C), 1.94 s (3H, MeC=C), 5.00-5.40 m (2H, 2C=CH), 5.56 m and 6.10 m (2H, C=CH ₂)
Vb	0.87-1.12 m (3H, Me), 1.18 s (6H, Me ₂ COO), 1.30-2.40 m [15H, 3CH, 2CH ₂ and 2(CH ₂) ₂], 1.43 s (6H, Me ₂ CC≡C), 1.57 s and 1.67 s (9H, CHMe and Me ₂ C=C), 5.00-6.00 m (2H, 2C=CH), 7.30-8.12 m (5H, Ph)
VIa	0.70-1.00 m (15H, 5Me), 1.00-2.05 m [15H, CH, 2CH ₂ , (CH ₂) ₂ and (CH ₂) ₃], 1.18 s (6H, Me ₂ COO), 1.40 s (9H, Me ₂ CC≡C and MeCC≡C), 1.92 s [3H, MeC=CC(O)], 5.47 m and 6.01 m (2H, C=CH ₂)
VIb	0.70-1.07 m (15H, 5Me), 1.07-2.15 m [13H, CH, 3CH ₂ and (CH ₂) ₃], 1.12 s (6H, Me ₂ COO), 1.45 s (9H, Me ₂ CC≡C and MeCC≡C), 7.30-8.10 m (5H, Ph)
VIIa	0.75-1.05 m (6H, 2Me), 1.20 s (6H, Me ₂ COO), 1.40-1.60 m [4H, (CH ₂) ₂], 1.50 s (6H, Me ₂ C), 1.90 s (3H, MeC=C), 1.95 q (2H, CH ₂), 3.85 m (6H, 2MeO), 5.52 m and 6.10 m (2H, C=CH ₂), 6.75-7.15 m (3H, 1,2,4-C ₆ H ₃)

Table 2. (Contd.)

Compd. no.	δ , ppm
VIIb	0.75–1.00 m (9H, 3Me), 1.12–1.70 m [14H, (CH ₂) ₂ and (CH ₂) ₅], 1.20 s (6H, Me ₂ COO), 1.50 s (6H, Me ₂ C), 2.05 q (2H, <u>CH</u> ₂ Me), 2.25 q [2H, CH ₂ C(O)], 3.86 m (6H, 2MeO), 6.70–7.15 m (3H, 1,2,4-C ₆ H ₃)
VIIc	0.89 t (6H, 2Me), 1.20 s (6H, Me ₂ COO), 1.45–1.60 m [4H, (CH ₂) ₂], 1.60 s (6H, Me ₂ C), 2.04 q (2H, CH ₂), 3.88 m (6H, 2MeO), 6.20–8.30 m (8H, 1,3,4-C ₆ H ₃ and Ph)
VIIIa	1.87 t (3H, <u>Me</u> CH ₂), 1.31 s (6H, Me ₂ COO), 1.25 s and 1.35 s (6H, Me ₂ CO), 1.46 s (6H, Me ₂ CC≡C), 1.47 q (2H, <u>CH</u> ₂ Me), 1.93 s (3H, MeC=C), 1.95–2.55 m (2H, CH ₂), 2.13 t (2H, <u>CH</u> ₂ CH ₂ O), 3.82 t (2H, CH ₂ O), 5.52 m and 6.06 m (2H, C=CH ₂)
VIIIb	0.77–0.94 m (6H, 2Me), 1.17 s (6H, Me ₂ COO), 1.15–1.70 m [20H, 2CH ₂ , (CH ₂) ₅ , Me ₂ CO], 1.77–2.37 m [4H, <u>CH</u> ₂ CH ₂ O and CH ₂ C(O)], 3.82 t (2H, CH ₂ O)
VIIIc	0.82 t (3H, Me), 1.15 s (6H, Me ₂ COO), 1.25 s and 1.38 s (6H, Me ₂ CO), 1.45 s (6H, Me ₂ CC≡C), 1.35–1.50 m [4H, (CH ₂) ₂ Me], 1.55–1.80 m (2H, CH ₂), 2.20 t (2H, <u>CH</u> ₂ CH ₂ O), 3.89 t (2H, CH ₂ O), 7.35–8.08 m (5H, Ph)
IXa	0.60–1.00 m (18H, 6Me), 1.00–2.25 m [30H, 6CH, CH ₂ , 4(CH ₂) ₂ , (CH ₂) ₃], 1.21 s (6H, Me ₂ COO), 1.49 s (6H, Me ₂ CC≡C), 2.09 s [3H, MeC(O)], 5.47 s and 6.21 s (1H, C=CH)
IXb	0.55–1.05 m (18H, 6Me), 1.05–2.20 m [30H, 6CH, CH ₂ , 4(CH ₂) ₂ and (CH ₂) ₃], 1.20 s (6H, Me ₂ COO), 1.48 s (6H, Me ₂ CC≡C), 1.89 s (3H, MeC=C), 5.49 m and 5.98 m (2H, C=CH ₂), 5.60 s and 6.43 s (1H, C=CH)
IXc	0.65–1.03 m (18H, 6Me), 1.03–2.25 m [30H, 6CH, CH ₂ , 4(CH ₂) ₂ , (CH ₂) ₃], 1.21 s (6H, Me ₂ COO), 1.52 s (6H, Me ₂ CC≡C), 5.47 s and 6.55 s (1H, C=CH), 7.25–8.25 m (5H, Ph)
X	0.75–1.05 m (9H, 3Me), 1.05–2.30 m [17H, 5CH, 2CH ₂ , 4(CH ₂) ₂], 1.20 s (6H, Me ₂ COO), 1.45 s (6H, Me ₂ CC≡C), 1.95 s (6H, 2MeC=C), 5.51 m and 6.05 m (4H, 2C=CH ₂)
XI	0.75–1.05 m (9H, 3Me), 1.05–2.40 m [17H, 5CH, CH ₂ and 5(CH ₂) ₂], 1.22 s (6H, Me ₂ COO), 1.47 s (6H, Me ₂ CC≡C), 1.96 s and 2.03 s [6H, 2MeC(O)]
XII	0.77–1.02 m (6H, <u>Me</u> CH ₂ and C ¹⁷ -Me), 1.02–2.20 m [17H, 3CH, CH ₂ and 3(CH ₂) ₂], 1.20 s (9H, Me ₂ COO and C ¹³ -Me), 1.41 s (3H, C ¹⁰ -Me), 1.52 s (6H, Me ₂ CC≡C), 1.91 s (6H, 2 <u>Me</u> C=CH ₂), 5.47 m and 6.04 m (4H, 2C=CH ₂), 5.05–6.50 m (3H, CH=CH and C=CH)
XIIIa	0.85 t (3H, <u>Me</u> CH ₂), 0.93 s (3H, C ¹³ -Me), 1.15 s (6H, Me ₂ COO), 1.45 s (6H, Me ₂ CC≡C), 1.05–2.95 m [17H, 3CH, CH ₂ and 3(CH ₂) ₂], 1.90 s and 2.03 s (6H, 2MeC=C), 5.50 m, 5.70 m, 6.02 m and 6.30 m (4H, 2C=CH ₂), 6.76–7.35 m (3H, H ^{1,2,4})
XIIIb	0.87 t [3H, <u>Me</u> (CH ₂) ₂], 0.95 s (3H, C ¹³ -Me), 1.19 s (6H, Me ₂ COO), 1.44 s (6H, Me ₂ CC≡C), 1.20–3.00 m [19H, 3CH and 4(CH ₂) ₂], 1.92 s and 2.06 s (6H, 2MeC=C), 5.51 m, 5.71 m, 6.04 m and 6.30 m (4H, 2C=CH ₂), 6.77–7.37 m (3H, H ^{1,2,4})
XIIIc	0.72–1.05 m (12H, 4Me), 1.05–2.95 m [41H, 3CH, CH ₂ , 3(CH ₂) ₂ , 2(CH ₂) ₆], 1.18 s (6H, Me ₂ COO), 1.47 s (6H, Me ₂ CC≡C), 6.72–7.35 m (3H, H ^{1,2,4})
XIII d	0.75–1.00 m (12H, 4Me), 1.20 s (6H, Me ₂ COO), 1.43 s (6H, Me ₂ CC≡C), 1.08–2.95 m [43H, 3CH, 4(CH ₂) ₂ and 2(CH ₂) ₆], 6.75–7.35 m (3H, H ^{1,2,4})
XIII e	0.82 t (3H, <u>Me</u> CH ₂), 1.05 s (3H, C ¹³ -Me), 1.19 s (6H, Me ₂ COO), 1.05–3.00 m [17H, 3CH, CH ₂ and 3(CH ₂) ₂], 1.45 s (6H, Me ₂ CC≡C), 6.88–8.25 m (13H, H ^{1,2,4} and 2Ph)
XIV	0.88 t (3H, <u>Me</u> CH ₂), 0.98 s (6H, Me ₂ CC=C), 1.18 s (6H, Me ₂ COO), 1.45 s (6H, Me ₂ CC≡C), 1.40–2.05 m [13H, OH, CH, CH ₂ , (CH ₂) ₃ , MeC=C], 5.55 d and 6.40 d (2H, CH=CH)
XVII	0.80–1.05 m [9H, <u>Me</u> (CH ₂) ₂ and Me ₂ CC=C], 1.19 s (6H, Me ₂ COO), 1.25–2.50 m [23H, OH, 3Me, 2(CH ₂) ₂ and (CH ₂) ₃], 1.47 s (6H, Me ₂ CC≡C), 5.53–6.72 m (3H, C=CH and CH=CH)
XVIII	0.87–1.02 m [9H, <u>Me</u> (CH ₂) ₂ and Me ₂ CC=C], 1.22 s (6H, Me ₂ COO), 1.82 s and 1.90 s (6H, 2MeC=C), 1.47 s (6H, Me ₂ CC≡C), Me ₂ CC≡C, 1.25–2.00 m [14H, 2(CH ₂) ₂ and (CH ₂) ₃], 5.00–6.67 m (5H, C=CH, CH=CH and C=CH ₂)

main substance. The column chromatography was performed on neutral Al_2O_3 , II grade Brockmann activity, eluent hexane, and on silica gel L 100/160 μ , eluent hexane, ether. The analysis for active oxygen by iodometry with the use of concn. HCl [10] gave overestimated results with the peroxides under study apparently due to the presence of a $\text{C}\equiv\text{C}$ bond. Cryoscopic measurement of molecular weights was carried out in benzene.

Initial peroxyalkynes **Ia**, **b**, and butyllithium were prepared by procedures [11, 12] respectively.

1-Methacryloyloxy-1-[6-methyl-4-(4-methylpent-3-enyl)cyclohex-3-enyl]-4-methyl-4-(2-methyl-2-pentylperoxy)pent-2-yne (Va), **1-benzoyloxy-1-[6-methyl-4-(4-methylpent-3-enyl)cyclohex-3-enyl]-4-methyl-4-(2-methylpentylperoxy)pent-2-yne (Vb)**, **2,3,8,8-tetramethyl-2-[1,4-dimethyl-1-methacryloyloxy-4-(2-methyl-2-pentylperoxy)pent-2-ynyl]-1,2,3,4,5,6,7,8-octahydronaphthalene (VIa)**, **2,3,8,8-tetramethyl-2-[1,4-dimethyl-1-benzoyloxy-4-*tert*-pentylperoxy-pent-2-ynyl]-1,2,3,4,5,6,7,8-octahydronaphthalene (VIb)**, **3,4-dimethoxy-1-[1-methacryloyloxy-4-methyl-4-(2-methyl-2-pentylperoxy)-1-ethylpent-2-ynyl]benzene (VIIa)**, **3,4-dimethoxy-1-[1-octanoyloxy-4-methyl-4-(2-methyl-2-pentylperoxy)-1-ethylpent-2-ynyl]benzene (VIIb)**, **3,4-dimethoxy-1-[1-benzoyloxy-4-methyl-4-(2-methyl-2-pentylperoxy)-1-ethylpent-2-ynyl]benzene (VIIc)**, **2,2-dimethyltetrahydro-4H-4-methacryloyloxy-4-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)pyran (VIIIa)**, **2,2-dimethyltetrahydro-4H-4-octanoyloxy-4-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)pyran (VIIIb)**, **2,2-dimethyltetrahydro-4H-4-benzoyloxy-4-[3-methyl-3-(2-methyl-2-pentylperoxy)but-1-ynyl]pyran (VIIIc)**, **3-acetoxy-3-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)cholest-4-ene (IXa)**, **3-methacryloyloxy-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)cholest-4-ene (IXb)**, **3-benzoyloxy-3-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)cholest-4-ene (IXc)** (general procedure). To a vigorously stirred solution of 0.006 mol of peroxyalkynes **Ia**, **b** in 20 ml of anhydrous ethyl ether was added within 0.5 h under argon at $-40\text{...}-20^\circ\text{C}$ 0.005 mol of butyl lithium in hexane solution. The reaction mixture was stirred for 1 h at the same temperature, and then 0.004 mol of aldehyde or ketone was added thereto. The cooling was removed, within 1–1.5 h the temperature of the reaction mixture was raised to ambient ($15\text{--}20^\circ\text{C}$), and the device was left overnight (for 18 h). To the formed solutions of lithium peroxyalcoholates **IV** at cooling to $0\text{--}5^\circ\text{C}$ was added while stirring 0.006 mol of carboxyl chloride, the cooling was removed, within 1–1.5 h

Table 3. UV spectra of compounds **Va**, **b**, **VIa**, **b**, **VII-IXa-c**, **X-XII**, **XIIIa-e**, **XIV-XVIII**

Compd. no.	λ_{max} , nm (ϵ)
Va	204 (15000)
Vb	203 (18000), 230 (18000)
VIa	208 (13000)
VIb	203 (12000), 231 (12000)
VIIa	208 (25000), 228 (13000), 275 (5000)
VIIb	206 (27000), 230 (11000), 271 (5000)
VIIc	205 (31000), 225 (26000), 270 (13000)
VIIIa	209 (9000)
VIIIb	205 (800)
VIIIc	202 (12000), 232 (14000)
IXa	205 (6000), 229 (6000), 270 (4000), 280 (3000)
IXb	210 (9000), 232 (9000), 270 (3000), 280 (3000)
IXc	202 (16000), 232 (14000), 268 (7000)
X	209 (16000)
XI	217 (3000)
XII	210 (28000), 250 (11000), 320 (3000)
XIIIa	210 (39000)
XIIIb	210 (38000)
XIIIc	205 (15000)
XIIId	205 (14000)
XIIIe	205 (30000), 230 (35000)
XIV	203 (6000), 239 (6000)
XV, XVI	310 (21000)
XVII	205 (10000), 244 (14000), 298 (3000)
XVIII	204 (9000), 309 (28000)

the temperature of the reaction mixture was raised to ambient ($15\text{--}20^\circ\text{C}$), and the device was left standing for 18 h. The reaction mixture was then diluted with 100 ml of petroleum ether, washed with water, with saturated water solution of NaHCO_3 , again with water, and dried with CaCl_2 . The solvent was removed, and the peroxides obtained were purified by column chromatography on Al_2O_3 (eluent hexane).

3,17 β -Dimethacryloyloxy-3-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)androstane (X), **3 β ,17-diacetoxy-17-[3-methyl-3-(2-methyl-2-pentylperoxy)but-1-ynyl]androstane (XI)**, **3,17 β -dimethacryloyloxy-3-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)-17 α -methylandrosta-1,4-diene (XII)**, **3,17-dimethacryloyloxy-17-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)estra-1,3,5(10)-triene (XIIIa)**, **3,17-dimethacryloyloxy-17-[3-methyl-3-(2-methyl-2-pentylperoxy)but-1-ynyl]estra-1,3,5(10)-triene (XIIIb)**,

3,17-dioctanoyloxy-17-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)estra-1,3,5(10)-triene (XIIIc), 3,17-dioctanoyloxy-17-[3-methyl-3-(2-methyl-2-pentylperoxy)but-1-ynyl]estra-1,3,5(10)-triene (XIIIId), 3,17-dibenzoyloxy-17-(3-methyl-3-*tert*-pentylperoxybut-1-ynyl)-estra-1,3,5(10)-triene (XIIIe) (general procedure). To a vigorously stirred solution of 0.006 mol of peroxyalkynes **Ia, b** in 20 ml of anhydrous tetrahydrofuran was added within 0.5 h under argon at $-40 \dots -20^\circ\text{C}$ 0.005 mol of butyllithium in hexane solution. The reaction mixture was stirred for 1 h at the same temperature, and then 0.002 mol of hydroxyketosteroid **III** was added thereto in 15 min in 10 ml of anhydrous tetrahydrofuran. The cooling was removed, within 1–1.5 h the temperature of the reaction mixture was raised to ambient ($15\text{--}20^\circ\text{C}$), and the reaction mixture was left standing for 18 h. To the formed solutions of lithium peroxyalcoholates **IV** at cooling to $0\text{--}5^\circ\text{C}$ was added while stirring 0.006 mol of carboxyl chloride, the cooling was removed, within 1–1.5 h the temperature of the reaction mixture was raised to ambient ($15\text{--}20^\circ\text{C}$), and the device was left standing for 18 h. The reaction mixture was then diluted with 100 ml of petroleum ether, washed with water, with saturated water solution of NaHCO_3 , again with water, and dried with CaCl_2 . The solvent was removed, and the peroxides obtained were purified by column chromatography on Al_2O_3 (eluent hexane).

2-Hydroxy-6-methyl-6-*tert*-pentylperoxy-1-(2,6,6-trimethylcyclohex-1-enyl)hept-1-en-4-yne (IV), 5-hydroxy-2-(2-methyl-2-pentylperoxy)-2,5,9-trimethyl-11-(2,6,6-trimethylcyclohex-1-enyl)undeca-6,8-dien-3-yne (XVII) (general procedure). To a vigorously stirred solution of 0.006 mol of peroxyalkynes **Ia, b** in 20 ml of anhydrous ethyl ether was added within 0.5 h under argon at $-40 \div -20^\circ\text{C}$ 0.005 mol of butyllithium in hexane solution. The reaction mixture was stirred for 1 h at the same temperature, and then 0.004 mol of a carbonyl compound was added thereto. The cooling was removed, within 1–1.5 h the temperature of the reaction mixture was raised to ambient ($15\text{--}20^\circ\text{C}$), and the reaction mixture was left standing for 18 h. The reaction mixture was then diluted with 100 ml of petroleum ether, washed with water, with saturated water solution of NaHCO_3 , again with water, and dried with CaCl_2 . The solvent was removed, and the peroxyalcohols obtained were purified by column chromatography on silica gel (eluent hexane–ether).

A mixture of 6-methyl-6-*tert*-pentylperoxy-1-(2,6,6-trimethylcyclohex-2-en-1-ylidene)hept-en-4-yne (XV) and 2-methyl-2-*tert*-pentylper-

oxy-1-(2,2-dimethyl-6-methylenecyclohex-1-ylidene)hept-2-en-4-yne (XVI), 2,9-dimethyl-2-(2-methyl-2-pentylperoxy)-5-methylene-11-(2,6,6-trimethylcyclohex-1-enyl)undeca-6,8-dien-3-yne (XVIII) (general procedure). To 0.003 mol of peroxyalcohol **XIV, XVII** in 5 ml of anhydrous ethyl ether at $0\text{--}5^\circ\text{C}$ was added within 2–3 min a solution of 0.1 ml of 57% HClO_4 in 3 ml of acetic anhydride. The reaction mixture was kept for 0.5 h at $0\text{--}5^\circ\text{C}$, then the temperature was raised to $20\text{--}23^\circ\text{C}$, and the mixture was left standing for 18 h. To the reaction mixture was added 50 ml of hexane, it was washed with water, saturated aqueous NaHCO_3 , and water till neutral, and then dried with MgSO_4 . The solvent was removed, and enyne peroxides (a mixture of compounds **XV** and **XVI**) were subjected to column chromatography on Al_2O_3 (eluent hexane).

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